The Photochemical Rearrangement of 5-Pyrazolidones

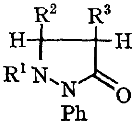
By SEYHAN N. EĞE

(*Department of Chemistry, University of Michigan, Ann Arbor, Michigan,* 48104)

DURING studies on the photochemistry of heterocyclic compounds,[1] 3-methyl-1-phenyl-5-pyrazolidone (Ia)[2] was found to undergo a novel ring contraction upon irradiation. Inspection of the i.r. spectrum of the crude mixture, formed by irradiation of (Ia) in methanol for 18 hr. in a Vycor tube with a Hanovia 450-w medium-pressure arc lamp, revealed that the original pyrazolidone was converted to the extent of 70—80% to a compound having its major carbonyl absorption ($CHCl_3$) at 1760 cm.$^{-1}$. The photoproduct, a thick oil, was separated from unchanged (Ia) by repeated chromatography on alumina and was further purified by Kugelrohr distillation. It was shown by analysis to be isomeric with (Ia). The n.m.r. spectrum of the compound had bands at δ(CCl_4), 1·15 (3H, d, *J* 6 c./sec.), 2·19 (1H, doublet of doublets, *J* 14·5 and 2 c./sec.), 2·73 (1H, doublet of doublets, *J* 14·5 and 5 c./sec.), 3·72 (1H, m), and 6·4—7·3 p.p.m. (6H, multiplet). The band positions and coupling constants in the n.m.r. spectrum are in good agreement with those determined for a series of β-lactams by Barrow and Spotswood.[3] This, and the distinctive position of the carbonyl absorption in the i.r. spectrum,[4] leads to the assignment of structure (IIa) to the photoproduct. The absorption of the proton on the exocyclic nitrogen in the n.m.r. as part of the broad aromatic multiplet is also in accordance with chemical-shift data reported for phenylhydrazides.[5,6]

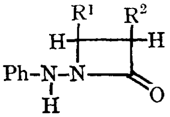
Irradiation of the isomeric 4-methyl-1-phenyl-5-pyrazolidone[7] under the same conditions gave similarly good conversion to a photoproduct (IIb), m.p. 85—87%, with carbonyl absorption in the i.r. ($CHCl_3$) at 1760 cm.$^{-1}$ and bands in its n.m.r. spectrum at δ(CCl_4) 1·23 (3H, d, *J* 7 c./sec.) 2·7—3·1 (2H, m), 3·36 (1H, t), and 6·4—7·2 p.p.m. (6H, m). 2,3-Dimethyl-1-phenyl-5-pyrazolidone (Ic)[2,8] on the other hand, is completely inert to irradiation under the conditions that lead to extensive rearrangement of (Ia) and (Ib).

Other well-authenticated cases of 1-aminoazetidin-2-ones do not appear in the literature. Sokolova and his colleagues[9,10] describe the formation of 1-dimethylaminoazetidin-2-ones in the reaction of 1,1-dimethylhydrazine with $\alpha\beta$-unsaturated acids and some of their derivatives. Unfortunately, the i.r. spectrum of only one compound, 1-dimethylamino-3-methylazetidin-2-one, m.p. 237—238°, is given.[9] The position of the carbonyl absorption band reported to be at 1578 cm.$^{-1}$ throws considerable doubt on the assignment of a β-lactam structure to this product. N.m.r. spectra,[10] taken at 40 Mc./sec., do not give sufficiently detailed information about this and the other products from these reactions to permit a more certain structural determination.



(I)

a; $R^1=R^3=H,H^2=Me$
b; $R^1=R^2=H,R^3=Me$
c; $R^1=R^2=Me,R^3=H$



(II)

a; $R^1=Me,R^2=H$
b; $R^1=H,R^2=Me$

(*Received, May 3rd*, 1968; *Com.* 549.)

---

[1] S. N. Eğe, *Chem. Comm.*, 1967, 488.
[2] L. Knorr and P. Duden, *Ber.*, 1892, **25**, 759.
[3] K. D. Barrow and T. M. Spotswood, *Tetrahedron Letters*, 1965, 3325.
[4] L. H. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen, London, 1958, pp. 214—215.
[5] P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 3502.
[6] H. E. Baumgarten, P. L. Creger, and R. L. Zey, *J. Amer. Chem. Soc.*, 1960, **82**, 3977.
[7] A. Vystrčil and Z. Stejskal, *Časopis Českého Lékárnictva*, 1950, **63**, 75 (*Chem. Abs.*, 1952, **46**, 7566d).
[9] T. A. Sokolova and L. A. Ovsyannikova, *Doklady Akad. Nauk S.S.S.R.*, 1962, **143**, 178.
[10] N. P. Zaperalova, T. A. Sokolova, N. M. Baghenov, and A. I. Kol'tsov, *Doklady Akad. Nauk S.S.S.R.*, 1963, **150**, 428.